

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification 7 : C07D 213/00, 231/00, 233/00, C07B 61/00</p> <p>(21) International Application Number: PCT/US99/28761</p> <p>(22) International Filing Date: 3 December 1999 (03.12.99)</p> <p>(30) Priority Data: 09/205,811 4 December 1998 (04.12.98) US</p> <p>(71) Applicant (for all designated States except US): SYMYX TECHNOLOGIES [US/US]; 3100 Central Expressway, Santa Clara, CA 95051 (US).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): MURPHY, Vince [US/US]; 20800 Homestead Road #11F, Cupertino, CA 95014 (US). HAGEMEYER, Alfred [DE/US]; Apt. J-302, 655 Fair Oaks Avenue, Sunnyvale, CA 94086 (US). POOJARY, Damodara, M. [IN/US]; 20677 Forge Way, Apartment 219, Cupertino, CA 95014 (US).</p> <p>(74) Agent: COPPOLA, Joseph, V., Sr.; Rader, Fishman & Grauer PLLC, Suite 140, 1533 North Woodward Avenue, Bloomfield Hills, MI 48304 (US).</p>		<p>(11) International Publication Number: WO 00/32572</p> <p>(43) International Publication Date: 8 June 2000 (08.06.00)</p> <p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p>
<p>Published Without international search report and to be republished upon receipt of that report.</p> <p>(54) Title: COMBINATORIAL DISCOVERY AND TESTING OF IONIC LIQUIDS</p> <p>(57) Abstract</p> <p>Arrays of ionic liquids are provided for combinatorial materials science research. These ionic liquids may be characterized by the general formula A⁺B⁻ where A⁺ represents any stable inorganic or organic cation and B⁻ represents any stable organic or inorganic anion. The uses for such arrays are as co-solvents in various chemical reactions.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COMBINATORIAL DISCOVERY AND TESTING OF IONIC LIQUIDS

5

This application is a continuation-in-part of pending U.S. patent application 09/205,811 filed December 4, 1998, which is incorporated herein by reference for all purposes.

10 FIELD OF THE INVENTION

The present invention relates to combinatorial materials science, specifically to libraries of ionic liquids and methods useful for the combinatorial research into the use and discovery of ionic liquids for a variety of reactions, including reactions where 15 the ionic liquid acts as a part of the reaction medium for the reaction. Combinatorial techniques are employed to test the compositions and methods of this invention.

BACKGROUND OF THE INVENTION

20 Combinatorial materials science generally refers to methods for creating a collection of diverse compounds or materials using a relatively small set of precursors and/or methods for rapidly testing or screening the collection of compounds or materials for desirable performance characteristics and properties. As currently practiced, combinatorial materials science permits scientists to systematically explore 25 the influence of structural variations in candidates by dramatically accelerating the rates at which they are created and evaluated. Compared to traditional discovery methods, combinatorial methods sharply reduce the costs associated with preparing and screening each candidate.

Combinatorial chemistry has revolutionized the process of drug discovery.

30 See, for example, 29 Acc. Chem. Res. 1-170 (1996); 97 Chem. Rev. 349-509 (1997); S. Borman, Chem. Eng. News 43-62 (Feb. 24, 1997); A. M. Thayer, Chem. Eng. News 57-64 (Feb. 12, 1996); N. Terret, 1 Drug Discovery Today 402 (1996).

One can view drug discovery as a two-step process: acquiring candidate compounds through laboratory synthesis or through natural product collection, followed by evaluation or screening for efficacy. Pharmaceutical researchers have long used high-throughput screening (HTS) protocols to rapidly evaluate the therapeutic value of

5 natural products and libraries of compounds synthesized and cataloged over many years. However, compared to HTS protocols, chemical synthesis has historically been a slow, arduous process. With the advent of combinatorial methods, scientists can now create large libraries of organic molecules at a pace on par with HTS protocols.

Recently, combinatorial approaches have been used for discovery programs

10 unrelated to drugs. For example, some researchers have recognized that combinatorial strategies also offer promise for the discovery of inorganic compounds such as high-temperature superconductors, magnetoresistive materials, luminescent materials, and catalytic materials. See, for example, co-pending U.S. patent application no. 08/327,513 "The Combinatorial Synthesis of Novel Materials"

15 (published as WO 96/11878), U.S. Patent No. 5,775,359 and co-pending U.S. patent application no. 08/898,715 "Combinatorial Synthesis and Analysis of Organometallic Compounds and Catalysts" (a version of which was published as WO 98/03251), each of which is herein incorporated by reference.

Ionic liquids are known. Ionic liquids are ionic compositions that are molten

20 at low temperature, which are sometimes referred to as molten salts. See Seddon, "Ionic Liquids for Clean Technology", J. Chem. Tech. Biotechnol., 68, pp. 351-356 (1997), incorporated herein by reference. Ionic liquids are known to form part of the reaction media for certain types of reactions. For example, Olivier and Chauvin, "Nonaqueous Room-Temperature Ionic Liquids: A New Class of Solvents for

25 Catalytic Organic Reactions", Chem. Ind. (Dekker) (1996), 68, pp. 249-263, incorporated herein by reference, disclose the use of ionic liquids for dimerization, alkylation, hydrogenation, metathesis, hydroformylation and other reactions. U.S. Patent No. 5,731,101, incorporated herein by reference, discloses use of ionic liquids for alkylation, arylation and polymerization reactions. U.S. Patent No. 5,304,615,

30 incorporated herein by reference, discloses use of ionic liquids as the catalyst for polymerization of an olefinic feedstock, which typically contains a mixture of monomers. See also WO 95/21872, WO 98/03454 and WO 95/21806, each of which is incorporated herein by reference. Similarly ionic compounds are known, see for

example Kawabata et al. Journal of Antibiotics, vol. 48, no. 9, pp. 1049-1051 (1995).

Ionic liquids are commercially available, for example from Solvent Innovation GmbH, Cologne, Germany.

Cationic polymerizations are also well known and are described in numerous publications. See, for example G. Odian, Principles of Polymerization (Wiley & Sons, 1991). Cationic polymerization of isoolefins, in particular isobutylene is also well documented. See, for example R. Faust, T. D. Shaffer, Cationic Polymerization (American Chemical Society, 1997). However, there are several disadvantages associated with the known processes, including the use of extremely low temperatures and the need to use polar, volatile solvents such as methyl chloride. There is clearly a need to develop new solvent systems and catalysts, which may be used at higher temperatures.

Despite all of the above, there remains a need to identify the ionic liquids that are commercially useful in particular reactions. For example, none of the cited references has shown the ability to polymerize isobutylenes into a very high molecular weight polymer using an ionic liquid, meaning polyisobutylenes having a weight average molecular weight (Mw) of over 100,000 using an ionic liquid. The difference between very low Mw polyisobutylenes (below about 3,000 Mw), low Mw polyisobutylenes (about 3,000-10,000 Mw), high Mw polyisobutylenes (between about 10,000-100,000 Mw) and very high Mw polyisobutylenes (above 100,000 Mw) is in the properties that such polymers may possess. Very low Mw polyisobutylenes are typically useful in adhesives, lubricants, motor oil and transmission fluids. Low Mw polyisobutylenes are useful in sealants and caulking applications. High Mw polyisobutylenes are useful in rubber products or as impact modifiers of thermoplastics. Very high Mw polyisobutylenes possess unique physical and chemical properties, such as low oxygen permeability and mechanical resilience, finding uses in the automobile industry as rubber products.

Also, the syntheses of very high molecular weight polyisobutylenes are not straightforward. For example, it is well known that to obtain very high Mw polyisobutylenes, extremely low temperatures must be employed in the polymerization reaction. Such temperatures are in the region of about -100 °C. See G. Odian, Principles of Polymerization (Wiley & Sons, 1991), pp. 396-398, incorporated herein by reference. Thus, the molecular weight of polyisobutylenes

produced typically increases as the temperature of the polymerization process decreases. However, U.S. Patent 5,304,615 states that when using ionic liquids as the polymerization medium for isobutylene, either alone or with comonomers, "contrary to expectations, the molecular weight of the product does not increase with decreasing 5 temperatures" (col. 4, lines 5-7). Finally, although U.S. Patent 5,304,615 states that polymers of Mw up to 100,000 can be formed (see Example 2), no one has demonstrated, until this invention, the ability to prepare very high Mw polyisobutylenes with an ionic liquid.

10 In addition, the discovery of which ionic liquids are most useful for which reactions is a particularly slow process.

SUMMARY OF THE INVENTION

15 Therefore it is an object of this invention to apply combinatorial techniques to the discovery of ionic liquids for particular reactions. The "combinatorialization" of ionic liquids can be performed by suitable combination of a group of cations with a wide selection of anions. The influence of the resulting solvent system that the employs the ionic liquid is systematically or randomly explored and the optimum 20 solvent or solvent mixture for the particular reaction of interest is identified. It is a further object to improve the efficiency of the research of ionic liquids to the discovery of new compositions for the preparation of polyisoolefins, and in particular very high molecular weight polyisobutylenes, improves the efficiency of discovery efforts. Further objects of this invention will be evident to those of skill in the art upon review of this specification.

25 In one aspect, this invention provides arrays of ionic liquids where each member of the array may be characterized by the general formula A^+B^- where A^+ represents any stable organic or inorganic cation and B^- represents any stable organic or inorganic anion. Each member of the array differs from other members of the array by having a different chemical composition. The array can be formed in plates that 30 contain a plurality of vials, with each vial holding a member of the array of the ionic liquids, such that each member of the array cannot contact another member of the array.

In another aspect, this invention relates to a method of testing ionic liquids in particular reactions, comprising providing an array of ionic liquids and running the reaction of interest in parallel using the ionic liquids in the array as a component in the reaction, such as the solvent, catalyst, etc. Different ionic liquid compositions can

5 be tested in the reaction of interest. Alternatively, each member of the array can contain the same ionic liquid allowing for process conditions of the reaction to be varied within the array. The reaction of interest can vary widely from combinatorial array to array, with the reactions of interest including cross-coupling, Friedel-Crafts, dimerization, oligomerization, polymerization, hydrogenation, oxidation,

10 dehydrogenation, aromatization, carbonylation, dehydromerization, hydrodehalogenation, hydrodesulfurization, oxychlorization, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylation, oxidative esterification, telomerization, hydroxylations of C=C bonds and aromatics, CH hydroxylation, oxidative cleavage, epoxidation, reduction, hydrosilylation and

15 hydroformylation.

In yet another aspect, this invention relates to the combinatorial testing of ionic liquids for the polymerization of olefins or isoolefins or for the copolymerization of an olefin or isoolefin plus additional comonomer. In this aspect, an array of ionic liquids is provided with an aliquot of each member of the array being

20 dispensed into a reactor block containing a plurality of reaction vessels. The other components of the polymerization reaction are added to the reactor vessels (e.g., monomer, catalyst, co-solvents, etc.) and the reaction is carried out in parallel at desired reaction conditions, which may be varied between two or more arrays or within a single array. The order of addition of reaction components depends on the

25 reaction being studied. In alternative embodiments, other compounds may be added to the ionic liquid to form a new catalyst composition, which polymerizes an isoolefin or copolymerizes the isoolefin plus additional comonomer.

In yet another aspect, this invention uses ionic liquids as a portion of the reaction medium for polymerizing of isoolefins into polyisoolefins in a combinatorial manner. In this aspect, the ionic liquid is part of a two or more phase solvent system, with the other portions of the solvent system comprising non-ionic liquids, such as alkanes (e.g., hexane, heptane), cycloalkanes (e.g., cyclohexane, methyl(cyclohexane), aromatics), Isopar E®, etc. Preferably in this embodiment, the

entire system is agitated to increase surface area between phases and where the system includes all solvents, catalysts, monomers, scavengers, etc. The miscibility of the two or more solvents can be adjusted by changing the components of the ionic liquid, such as by varying the chain length of a hydrocarbon portion of the cation or 5 anion in the ionic liquid.

Other aspects of this invention include methods of making arrays of ionic liquids using liquids handling robots or other methods and methods of running reactions in parallel with ionic liquids.

10

DETAILED DESCRIPTION OF THE INVENTION

The phrases "characterized by the formula" or "represented by the formula" are used in the same way that "comprising" is commonly used. The term "independently selected" is used herein to indicate that the R groups, e.g., R¹, R², and 15 R³, can be identical or different (e.g. R¹, R² and R³ may all be substituted alkyls or R¹ and R² may be a substituted alkyl and R³ may be an aryl, etc.). A named R group will generally have the structure that is recognized in the art as corresponding to R groups having that name. For the purposes of illustration, representative R groups as enumerated above are defined herein. These definitions are intended to supplement 20 and illustrate, not preclude, the definitions known to those of skill in the art.

The term "catalyst" is used herein to include all forms of catalysis, including classic initiators, co-initiators, co-catalysts, activating techniques, etc. For example, if an organometallic compound has a cationic charge, initiating a cationic polymerization in an ionic liquid, the organometallic will be referred to as a catalyst 25 herein. Similarly, if the organometallic compound or complex operates in a coordination mechanism, it will still be referred to herein as a catalyst.

The term "hydrocarbyl" is used herein to refer to a radical having only carbon and hydrogen atoms, including, e.g., alkyl and the like.

The term "alkyl" is used herein to refer to a branched or unbranched, saturated 30 or unsaturated, monovalent hydrocarbon radical. When the alkyl group has from 1-6 carbon atoms, it is referred to as a "lower alkyl." Suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. In particular embodiments, alkyls have between 1 and

200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

“Substituted alkyl” refers to alkyl as just described including one or more groups such as lower alkyl, aryl, acyl, halogen (i.e., alkylhalos, e.g., CF₃), hydroxy, amino, phosphido, alkoxy, alkylamino, acylamino, acyloxy, aryloxy, aryloxyalkyl, 5 mercapto, both saturated and unsaturated cyclic hydrocarbons, heterocycles and the like. These groups may be attached to any carbon of the alkyl moiety.

The term “aryl” is used herein to refer to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety.

10 The common linking group may also be a carbonyl as in benzophenone. The aromatic ring(s) may include substituted or unsubstituted phenyl, naphthyl, biphenyl, diphenylmethyl and benzophenone among others. In particular embodiments, aryls have between 1 and 200 carbon atoms, between 1 and 50 carbon atoms or between 1 and 20 carbon atoms.

15 “Substituted aryl” refers to aryl as just described including one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, phosphido, alkoxy, alkylamino, acylamino, acyloxy, mercapto and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The linking group 20 may also be a carbonyl such as in cyclohexyl phenyl ketone. Specific examples of substituted aryl groups include -C₆F₅ and -C₆H₃(CF₃)₂.

The term “acyl” is used to describe a substituted carbonyl substituent, --C(O)J, where J is alkyl or substituted alkyl, aryl or substituted aryl as defined herein.

25 The term “amino” is used herein to refer to the group -NJJ', where J and J' may independently be hydrogen, alkyl, substituted alkyl, aryl, substituted aryl or acyl.

The term “alkoxy” is used herein to refer to the --OJ group, where J is an alkyl, substituted lower alkyl, aryl, substituted aryl, wherein the alkyl, substituted alkyl, aryl, and substituted aryl groups are as described herein. Suitable alkoxy radicals include, for example, methoxy, ethoxy, phenoxy, substituted phenoxy, 30 benzyloxy, phenethoxy, t-butoxy, etc.

As used herein, the term “phosphino” refers to the group -PJJ', where J and J' may independently be hydrogen, alkyl, substituted alkyl, aryl, substituted aryl or acyl.

As used herein, the term “mercapto” defines moieties of the general structure

J—S—J' wherein J and J' are the same or different and are hydrogen, alkyl, aryl or unsubstituted or substituted heterocyclic as described herein.

The term "saturated cyclic hydrocarbon" denotes groups such as cyclopropyl, cyclobutyl, cyclopentyl, etc. and substituted analogues of these structures.

5 The term "unsaturated cyclic hydrocarbon" is used to describe a monovalent nonaromatic group with at least one double bond, such as cyclopentene, cyclohexene, etc. and substituted analogues thereof.

10 The term "heteroaryl" as used herein refers to aromatic rings in which one or more carbon atoms of the aromatic ring(s) are substituted by a heteroatom such as nitrogen, oxygen or sulfur. Heteroaryl refers to structures that may be a single aromatic ring, multiple aromatic ring(s), or one or more aromatic rings coupled to one or more nonaromatic ring(s). In structures having multiple rings, the rings can be fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in phenyl
15 pyridyl ketone. As used herein, rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "heteroaryl."

20 "Heteroarylalkyl" defines a subset of "alkyl" wherein the heteroaryl group is attached through an alkyl group as defined herein. For example, if R² is a heteroarylalkyl, the alkyl portion will be bonded to the atom from which R² emanates and the heteroaryl portion will be a "substituent" on the alkyl.

25 "Substituted heteroaryl" refers to heteroaryl as just described wherein the heteroaryl nucleus is substituted with one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc. Thus, substituted analogues of heteroaromatic rings such as thiophene, pyridine, isoxazole, phthalimide, pyrazole, indole, furan, etc. or benzo-fused analogues of these rings are defined by the term "substituted heteroaryl."

30 "Substituted heteroarylalkyl" refers to a subset of "substituted alkyls" as described above in which an alkyl group, as defined herein, links the heteroaryl group to the bonding point on the ligand.

The term "heterocyclic" is used herein to describe a monovalent saturated or unsaturated nonaromatic group having a single ring or multiple condensed rings from 1-12 carbon atoms and from 1-4 heteroatoms selected from nitrogen, phosphorous

sulfur or oxygen within the ring. Such heterocycles are, for example, tetrahydrofuran, morpholine, piperidine, pyrrolidine, etc.

The term "substituted heterocyclic" as used herein describes a subset of "heterocyclics" wherein the heterocycle nucleus is substituted with one or more functional groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

The term "heterocyclicalkyl" defines a subset of "alkyls" wherein an alkyl group, as defined herein, links the heterocyclic group to the bonding point on the molecule.

The term "substituted heterocyclicalkyl" defines a subset of "heterocyclic alkyl" wherein the heterocyclic nucleus is substituted with one or more groups such as alkyl, acyl, halogen, alkylhalos (e.g., CF₃), hydroxy, amino, alkoxy, alkylamino, acylamino, acyloxy, mercapto, etc.

The term "scavenger" is used herein to mean a compound that does not substantially interfere with the reaction, but reacts with impurities or undesired species that may be present in the system. A "scavenger" is intended to refer to a compound that increases catalyst activity presumably by reacting with impurities or undesired species.

Additionally, abbreviations used herein include: Ph = C₆H₅, Me = methyl, Et = ethyl, Prⁱ = isopropyl, TMS = trimethylsilyl, Mes = 2,4,6-Me₃C₆H₂, Fc = ferrocene, Bu^t = tertiary butyl, DMAT = o-dimethylaminotoluene, DME = dimethoxyethane, and TFA = trifluoroacetate.

The term "polyisobutylenes" is used herein to refer to either homopolymers of isobutylene or copolymers of isobutylene and a suitable comonomer, which include acrylates, methacrylates, acrylonitriles, C₄-C₂₀ butadienes, C₄-C₇ isoolefins, C₄-C₁₂ diolefins, C₄-C₁₂ conjugated diolefins, cationically polymerizable aromatics (such as indene and fulvenes) and styrene (each of which can be substituted or unsubstituted). More specific comonomers included within the definition of polyisobutylenes include those selected from the group consisting of piperylene, 2,3-dimethylbutadiene, 2,4-dimethyl-1,3-pentadiene, cyclopentadiene, methylcyclopentadiene, limonene, 1,3-cyclohexadiene, norbornadiene, isoprene, 1-butene, 2-butene, norbornene and combinations thereof.

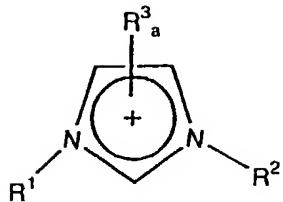
The ionic liquids in the array(s) of this invention may be characterized by the general formula A^+B^- where A^+ is a cationic organic or inorganic molecule and B^- is an anionic organic or inorganic molecule. In some embodiments, A^+ can be linked to B^- forming a zwitterion. The mole fractions of A^+ and B^- in the ionic liquid may be varied to suit the reaction being studied. See for example, *J. Chem. Tech.*

Biotechnol., 68, pp. 351-356 (1997), incorporated herein by reference. Mole fractions of A^+ and B^- in the ionic liquid are one variable that may be changed between members of the array of ionic liquids.

Many unsubstituted or substituted heterocyclic ring system may be converted into a stable cation A^+ through the process of alkylation or protonation or acylation or another method known to those of skill in the art. See for example T.L. Gilchrist "Heterocyclic Chemistry" (Wiley & Sons, 1995). Examples of unsubstituted or substituted heterocyclic ring systems that may converted into stable organic cations useful to this invention may be found in the Ring Systems Handbook (publication of the Chemical Abstracts Service 1993 Edition). These include (but are not limited to): imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines, quinoxalines, quinolines, isoquinolines, thazines, oxazines, azaannulenes and the like.

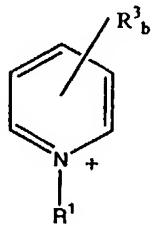
In addition, acyclic organic systems are also suitable and may be converted into stable organic cations A^+ in a similar manner. Examples include, but are not limited to amines (including amidines, imines, guanidines and the like), phosphines (including phosphinimines and the like), arsines, stibines, ethers, thioethers, selenoethers and the like.

In some embodiments, A^+ can be characterized by the general formula:



where R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, 5 substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2 or 3 signifying the number of R^3 groups attached to a carbon atom of the ring. In a preferred embodiment, R^1 is ethyl and R^2 is methyl.

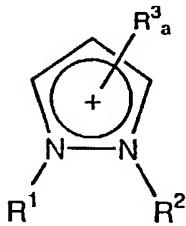
In other embodiments, A^+ can be characterized by the general formula:



10

where R^1 and R^3 are as defined above and b is 0, 1, 2, 3, 4 or 5 signifying the number of R^3 groups attached to a carbon atom of the ring.

In other embodiments, A^+ can be characterized by the general formula:



15 where R^1 , R^2 , R^3 and a are as defined above.

In yet further embodiments, A^+ can be characterized by the either of the general formulas: $R^1R^2R^3R^4N^+$ or $R^1R^2R^3R^4P^+$ where each of R^1 , R^2 , R^3 and R^4 is

12

independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

5 In more specific embodiments, B^- may be represented by the general formula $AlR_{4-z}X_z^-$ where R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

10 X is selected from the group of halogens (e.g., Cl, F, I and Br); and z is 0, 1, 2, 3 or 4. In other embodiments B^- may be selected from the group consisting of halogens, JX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , JR_4^- (where R is as defined above, X is as defined above and J is boron), substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites,

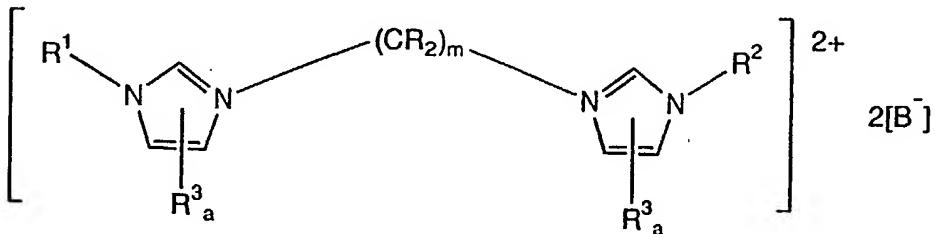
15 polyoxometallates, substituted or unsubstituted carboxylates and triflates. B^- may also be a non-coordinating anion; see U.S. Patent 5,599,761, incorporated herein by reference. In many heterogeneous applications, B^- is an inorganic anion, such as $Al_2Cl_7^-$, Cl^- , JF_4^- (where J is boron), PF_6^- , $AlCl_4^-$ or a metal-organic anion.

20 In an alternative embodiment, an ionic liquid may comprise multiply charged cations or multiply charged anions, or both. For example:



where n is any positive integer greater than 1.

25 One example of an ionic liquid using a multiply charged ion is one that uses an imidazolium cation that may be represented by the following general formula:

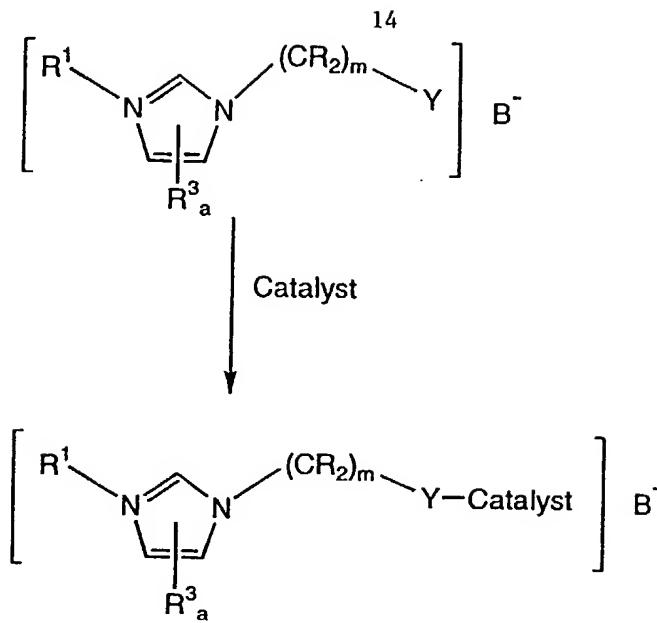


where R, R¹, R², R³ and a are as defined above, and m is an integer from 1-50. This example is depicted with an alkyl chain connecting the two-imidazolium moieties, but other connecting chains may also be used, such as substituted alkyls, substituted aryls and the like. Ionic liquids containing other multiply charged systems can also be used, including multiply charged cations prepared from the other unsubstituted or substituted heterocyclic ring systems or acyclic systems described above. Ionic liquids containing multiply charged ions may be mixed with ionic liquids containing singly charged ions to form useful catalyst combinations.

The ionic liquids used in this invention may be combined with reagents that may initiate cationic polymerizations, such as, but not limited to JR_{3-y}X_y, AlR_{3-y}X_y, alkylaluminoxanes, GaR_{3-y}X_y, InR_{3-y}X_y, TiR_{4-z}X_z, In(triflate)₃, Ge[NR₂]₂, SnR_{4-z}X_z, VCl₃, VCl₄, VOCl₃, VOCl₂, Sc(triflate)₃, Yb[NR₂]₃, Ti(OPrⁱ)₄, CpTiMe₃, Cp₂TiR₂, Cp₂ZrR₂, Cp₂HfR₂, TiCl₃, ZrCl₃, HfCl₃, ZrCl₄, HfCl₄, Ti[(NR₂)_{4-z}R_z], Zr[(NR₂)_{4-z}R_z], Hf[(NR₂)_{4-z}R_z], Zr[(NR₂)_{4-z}X_z], Hf[(NR₂)_{4-z}X_z], Ti[(NR₂)_{4-z}X_z], La[NR₂]₂, Er[NR₂]₂, ThCl₄, ThOCl₂, UCl₄, UCl₅, Cp₃U, NbCl₅, TaCl₅, CrCl₂, Cr(TFA)₂, CrCl₃, Cr(TFA)₃, CrOCl₂, CrO₂Cl₂, CrO₃, Cp₂Cr, MoCl₃, MoCl₄, MoCl₅, WCl₃, WCl₄, FeCl₂, Fe(TFA)₂, FeCl₃, Fe(TFA)₃, Co(TFA)₂, Co(TFA)₃, Mn(TFA)₂, Ni(TFA)₂, Pd(TFA)₂, V(TFA)₃, V(TFA)₂, Cu(TFA), Ag(TFA), SbX₅, PX₅, PX₃, POX₃, Cp₂AlR, HX, RX, water, alcohols, triflic acids, substituted or unsubstituted carboxylic acids, acylium ions, substituted alkyls, substituted aryls, [Ph₃C][JR₄], [R₃NH][JR₄], [R₂OH][JR₄], [Ph₃C][JX₄], [Ph₃C][PF₆], [Ph₃C][SbF₆], [Ph₃C][AsF₆], NaJR₄, LiJR₄, KJR₄, AgJX₄, AgJR₄, AgPF₆, AgSbF₆, AgAsF₆, AgNO₃, PbJX₄, PbJR₄, PbPF₆, PbSbF₆, PbAsF₆, PbNO₃, TiJR₄, TiPF₆, TiJX₄, TiSbF₆, TiAsF₆, TiNO₃ and any combinations thereof.

In the above list, R is defined as above; J is boron; y is a number 0, 1, 2 or 3; z is a number 0, 1, 2, 3 or 4; Cp is an unsubstituted or substituted cyclopentadienyl ring, substituted or unsubstituted indenyl, substituted or unsubstituted fluorenyl and the like such as bridging version of cyclopentadienyl, idenyl and fluorenyl complexes; X is a halogen, such as Cl, Br, I or F. Other initiators known to those skilled in the art may also be suitable.

In another alternative embodiment, the ionic liquid of this invention may contain a functional group, for example, that can act as a catalyst or scavenger. For example, the functional group may be attached directly to the cationic portion of the ionic liquid, such as is represented by the following general formula:

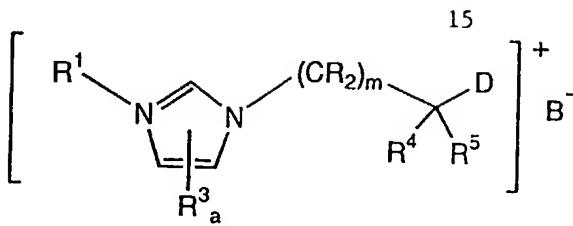


where R, R¹, R³, a and m are as defined above, and Y is any functional group. In a preferred embodiment Y is capable of binding the catalyst or scavenger to a

5 component of the ionic liquid. Alternatively, the catalyst or scavenger may be joined to the anion

(B⁻) in a similar manner. In the example above an alkyl chain is used to tether the catalyst to the organic cation. Other tethers are known and may be used in this embodiment, such as those that are discussed in U.S. patent application no.

10 09/025,841, filed February 19, 1998, incorporated herein by reference. In this embodiment other stable ionic liquids can also be used, including ionic liquids containing multiply charged systems and ionic liquids comprising cations prepared from the other unsubstituted or substituted heterocyclic ring systems or acyclic systems described above. Additionally, functionalized ionic liquids from this
 15 embodiment may be combined with non-functionalized ionic liquids (containing singly or multiply charged ions) to form useful catalyst compositions. Ionic liquids from this embodiment may be combined with a catalyst or scavenger or any combination thereof to form a useful catalyst composition. An example of an ionic liquid of this embodiment is:



where R, R¹, R³ a and m are as defined above; and R⁴ and R⁵ are defined as R¹ is defined above and D may be any halogen, SCN, CN, OH, OR, OCOR, COOR, O₂SR.

5 This ionic liquid may be combined with a catalyst (and/or optionally a scavenger) such as those listed above to form useful catalyst compositions capable of preparing very high molecular weight polyisobutylenes.

The ionic liquids of this invention may be made by methods known to those of skill in the art. See for example, U.S. Patent No. 5,731,101 and WO 95/21871, both 10 of which are incorporated herein by reference.

The ionic liquids of this invention can be catalysts alone, or may be combined with other compounds to form new catalytic compositions. Organometallic complexes may be added to the ionic liquids, with such complexes being any of those disclosed in commonly owned U.S. patent application no. 08/898,715, filed July 22, 15 1997, incorporated herein by reference. The catalysts useful with the ionic liquids are those that initiate a cationic polymerization reaction, including those listed above. See also WO 95/29940, incorporated herein by reference. Other mechanisms besides cationic polymerization may be at work in the presence of an organometallic complex, which may or may not have a charge. This specification is not limited to a 20 cationic mechanism in conjunction with polymerization reactions.

The presence of the ionic liquid will have an effect on the polarity of polymerization mixture. Thus, depending on the type of process employed, the structure, yield, selectivity, molecular weight, etc. of the polymer product formed can vary. Since the ionic liquid can solubilize compounds that are ordinarily insoluble in 25 organic solvents (e.g., metal complexes), the products can be readily separated from the ionic liquid, for example by decanting. Thus, this invention provides an easy method for removing product polymers from unwanted catalyst and avoiding additional ashing procedures for the removal of catalysts from polymer products. Therefore, this invention anticipates that novel polymers, copolymers or

16

interpolymers may be formed as a result of the processes of this invention, including polymers having unique physical and melt flow properties. Such polymers can be employed alone or with other polymers in a blend to form products that may be molded, cast, extruded or spun.

5 Polymerization can be carried out in a cationic process or in the Ziegler-Natta or Kaminsky-Sinn methodology, including temperatures of from -100°C to 400°C and pressures from atmospheric to 3000 atmospheres. Thus, the ionic liquids may serve only as the solvent for an organometallic compound or complex, which acts as the catalyst. There are numerous examples of catalytic organometallic complexes, such
10 as mono-cyclopentadienyl or bis-cyclopentadienyl complexes. The organometallic compounds may be active catalysts or may be combined with an activator. When an activator or activating technique is used, those of skill in the art may use alumoxanes, strong Lewis acids, compatible noninterfering activators and combinations of the foregoing. See U.S. Patents 5,599,761, 5,616,664, 5,453,410, 5,153,157 and
15 5,064,802. Suspension, solution, slurry, gas phase or high-pressure polymerization processes may be employed with the catalysts and compounds of this invention. Such processes can be run in a batch, semi-batch or continuous mode. Examples of such processes are well known in the art. A support for the catalyst may be employed, which may be alumina, silica or a polymers support. Methods for the preparation of
20 supported catalysts are known in the art. Slurry, suspension, solution and high-pressure processes use a suitable solvent as known to those skilled in the art.

 In another embodiment, the ionic liquids of this invention form a portion of the reaction medium by mixing the ionic liquid with one or more co-solvents. Typically, this means that a two-phase solvent mixture is used for the reaction.
25 Vigorous mixing is typically employed in this embodiment, but it is possible that proper selection of the ionic liquid and co-solvent(s) will mean that such mixing is not required. For example, the miscibility of the ionic liquid with the one or more co-solvents may result in a solvent system that does not appear to be a two phase solvent system. The miscibility of the ionic liquid with the co-solvent(s) can be adjusted by
30 changing R, R¹, R² or R³ in the above formulas for the ionic liquids to be more compatible with the co-solvent. For example if R is a long chain alkane, the ionic liquid will be more miscible with a hexane co-solvent. A long chain alkane is considered to be a C₁₀-C₁₀₀ alkyl, for example. Co-solvents can be selected from the

group consisting of alkanes, substituted alkanes, aromatics and substituted aromatics. The use of a mixed solvent system (i.e., ionic liquid and co-solvent) may increase the solubility of certain organometallic complexes. See, Chauvin et al., *Ind. Eng. Chem. Res.*, Vol 34, No. 4, pp. 1149-1155 (1995).

5 Other Reactions useful to this invention include but are not limited to certain other organic transformations, such as cross-coupling reactions (e.g., Suzuki, Heck, aminations, Negishi, Meyers, Stille etc.), Friedel-Crafts, dimerization, oligomerization and polymerization reactions (e.g., Ziegler-Natta catalysts and other single-site coordination catalysts such as metallocenes may be used in the presence of an ionic 10 liquids) as well as the other reactions listed herein.

For example, ionic liquids can be used to form two phases, leading to a large 15 number of organic product mixtures useful in heterogeneous catalysis. In many cases this leads to a bi-phasic system which allows easy product separation and catalyst recycling. The lack of vapor pressure allows convenient removal of products through 20 distillation. Of particular interest to catalysis are metal catalyzed reactions either by oxidized metals (e.g. Pd^{2+}) or by reduced metals (e.g. $Pd^{(0)}$). These metals could be in homogeneous solution or immobilized/heterogenized onto a support. Reduced metals can be unsupported (e.g., Pd black, nanoparticles, clusters, colloids) or supported (e.g., Pd/C). Metal ions can be reduced or activated in-situ in the ionic liquid (e.g., by 25 contacting with a gaseous reducing agent). By proper choice (or high throughput screening of arrays of ionic liquids) of cations and anions the catalyst performance can be improved. For instance, the selection of anions ranges from basic, coordinating anions like Cl^- to acidic, non-coordinating anions like $Al_2Cl_7^-$ (as discussed above). The anions may have a significant role in the reactivity of the metal 30 catalyst. In addition by adding co-solvents or modifiers the reactivity of the catalytic metal can be further enhanced. For example, transferring its coordinating Cl^- ligands to a Lewis acid can activate Pd ions. This process creates vacant sites in the coordination sphere of Pd ions for the interaction and activation of substrate species.

Thus, in general any catalyzed reactions using ionic liquids as at least part of 35 the reaction media in a combinatorial format is part of this invention. Each of the candidate materials (e.g., catalysts) being screened for a capability to enhance a chemical process of interest (e.g., a chemical reaction) can be an element, a compound or a composition comprising a plurality of elements and/or compounds.

The candidate materials can be in a gaseous, liquid or solid phase. Solid-phase materials are preferred for some applications. The particular elements, compounds or compositions to be included in a library of candidate materials will depend upon the particulars of the chemical process being investigated. However, the particular 5 chemical process being investigated is not critical, and can include chemical reactions and chemical separations, among others.

The chemical process is preferably a chemical reaction, which for purposes hereof, means a process in which at least one covalent bond of a molecule or compound is formed or broken. As such, immunoreactions in which immunoaffinity is based solely 10 on hydrogen bonding or other forces – while chemical processes – are not considered to be chemical reactions. In general, the candidate materials of this invention catalyze reactions that include activation of, breaking and/or formation of H-Si, H-H, H-N, H-O, H-P, H-S, C-H, C-C, C=C, C≡C, C-halogen, C-N, C-O, C-S, C-P, C-B and C-Si bonds among others. Exemplary chemical reactions for which reaction-enhancing 15 materials may be identified according to the present invention include, without limitation, hydrogenation, oxidation, dehydrogenation, aromatization, carbonylation, dehydromerization, hydrodehalogenation, hydrodesulfurization, oxychlorination, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylations, oxidative esterification, telomerization, hydroxylations of C=C bonds 20 and aromatics, CH hydroxylation, oxidative cleavage, epoxidation, reduction, hydrogenation, dehydrogenation (including transfer hydrogenation), hydration, dehydration, hydrosilylation, hydrocyanation, hydroformylation (including reductive hydroformylation), carbonylation, hydrocarbonylation, amidocarbonylation, hydrocarboxylation, hydroesterification, hydroamination, hetero-cross-coupling 25 reaction, isomerization (including carbon-carbon double bond isomerization), dimerization, trimerization, polymerization, co-oligomerization (e.g. CO/alkene, CO/alkyne), co-polymerization (e.g. CO/alkene, CO/alkyne), insertion reaction, aziridation, metathesis (including olefin metathesis), carbon-hydrogen activation, cross coupling, Friedel-Crafts acylation and alkylation, Diels-Alder reactions, C-C 30 coupling, Heck reactions, arylations, Fries rearrangement, vinylation, acetoxylation, aldol-type condensations, aminations, reductive aminations, hydrodechlorinations, hydrodesulfurations and Fischer-Tropsch reactions, asymmetric versions of any of the aforementioned reactions, and combinations of any of the aforementioned reactions in

19

a complex reaction sequence of consecutive reactions. For chemical reactions, the candidate materials can be generally classified as those materials which are chemically altered or consumed during the course of the reaction (e.g., co-reactant materials, cataloreactants) and those materials which are not chemically altered or 5 consumed during the course of the reaction (e.g., catalysts, selective blocking moieties). In preferred applications, the candidate materials are catalysts. As used herein, the term catalyst is intended to include a material that enhances the reaction rate of a chemical reaction of interest or that allows a chemical reaction of interest to proceed where such reaction would not substantially proceed in the absence of the 10 catalyst.

The candidate materials preferably comprise elements or compounds selected from the group consisting of inorganic materials, metal-ligands and non-biological organic materials. In some applications, the candidate materials will consist essentially of inorganic materials, consist essentially of metal-ligand materials, or 15 consist essentially of non-biological organic materials. Moreover, in some applications, the candidate materials will be compositions comprising mixtures of inorganic materials, metal-ligand materials, and/or non-biological organic materials in the various possible combinations.

Inorganic materials include elements (including carbon in its atomic or 20 molecular forms), compounds that do not include covalent carbon-carbon bonds (but which could include carbon covalently bonded to other elements, e.g., CO₂), and compositions including elements and/or such compounds. Inorganic candidate materials that could be investigated according to the approaches described herein include, for example: noble metals such as Au, Ag, Pt, Ru, Rh, Pd, Ag, Os and Ir; 25 transition metals such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Hf, Nb, Mo, Ta, W and Re; rare-earth metals such as La, Ce, Pr, Nd, Sm, Eu, Tb, Th, Dy and U; alloys of noble metals, transition metals and/or rare-earth metals; metal oxides such as CuO, NiO and Co₃O₄; noble-metal-doped metal oxides such as noble-metal-doped CuO, NiO and Co₃O₄; multi-metal oxides such as binary oxides of Cu-Cr, Cu-Mn, Cr-Mn, 30 Ni-Cr, Ni-Mn, Ni-Cu, Ni-Mo, Cu-Mo, Ni-Co, Co-Mo, Ni-Fe, Fe-Mo, Cu-Fe, Mn-Ag, Mn-Sn, Ag-Sn, Cu-Ag, Cu-V, Ag-V, Cu-V, Ni-V, Bi-Mo, Bi-V, Mo-V, V-Zr, V-Ti, Zr-Ti, V-Nb, Nb-Mo, V-P, P-Mo, Ni-P, P-Cu, Co-P, Co-Fe, P-Fe, Mg-V, Mg-Sn, V-Sn, K-Ti, K-Bi, Ti-Bi, Cr-Sb, Cr-V, Sb-V, Bi-Mo, Bi-Nb, K-Cr, K-Al, Al-Cr, Zn-Cu,

20

Zn-Al, Cu-Al, La-Cr, La-Zr, Cr-Zr, La-Mo, Mo-Zr, La-W, W-Zr, Mo-W, W-V, Cu-W, Bi-W, Fe-Sb, Fe-V and Ni-Ta, Ni-Nb and Ta-Nb, and such as ternary oxides of Cu-Cr-Mn, Ni-Cr-Mn, Ni-Cu-Mo, Ni-Co-Mo, Ni-Fe-Mo, Cu-Fe-Mo, Mn-Ag-Sn, Cu-Ag-V, Cu-Ni-V, Bi-Mo-V, V-Zr-Ti, V-Nb-Mo, V-P-Mo, Ni-P-Cu, Co-P-Fe, Mg-V-
5 Sn, K-Ti-Bi, Cr-Sb-V, Bi-Mo-Nb, K-Cr-Al, Zn-Cu-Al, La-Cr-Zr, La-Mo-Zr, La-W-Zr, Mo-W-V, Cu-Mo-W, Bi-Mo-W, Bi-V-W, Fe-Sb-V and Ni-Ta-Nb; metal carbides such as MoC, WC, PdC; metal sulfates, metal sulfides, metal nitrides, metal carbonates, metal chlorides, metal acetates, polyoxometallates (POM); metal phosphates such as vanadylpyrophosphates (VPO); Bronstead acids such as HF;
10 Lewis Acids such as AlCl_3 ; and mixtures of any of the aforementioned inorganic materials, among others. Exemplary inorganic material libraries could include, for example, a triangular-shaped array of ternary metal oxides (e.g. such as oxides of the ternary metal partners described above) with single metal oxide compounds at each corners, binary metal oxide compositions along each of the sides with varying ratios
15 of constituents, and ternary metal oxide compositions in the interior regions of the triangular array with varying ratios of constituents.

Quaternary rectangle-shaped arrays of metal oxides having 4 metals in each well and ternaries as the edges can be used. The inorganic materials do not have to be in the solid state to be catalytically active, although in many embodiments the
20 materials will be in the solid state. Homogeneous solutions of atomically dispersed metal ions with inorganic, simple substituents (as opposed to complex ligands) and anionic counterions are one embodiment of the invention. The precursor can be a soluble solid salt of the metal or a stock solution. Examples are $\text{Pd}(\text{OAc})_2$, $\text{Pd}(\text{NO}_3)_2$, PdCl_2 , and PdSO_4 . Redox active metals like the soluble salts of V, Cr, Mn, Fe, Co,
25 Ni, Cu, Pd, Pt, Os, Rh, Re, Ru, Ce and Lewis acidic metals, like Al, B, Ga, Ge, Sn, Sb, Ir, Re, the rare earths, Ti, Zr, Zn, Fe, W, Mo are most common. Anions are simple and available like acetate, nitrate, sulfate, chloride, and oxalate. Libraries of inorganic candidate materials can be prepared, for example, according to the methods disclosed in U.S. Patent No. 5,776,359 to Schultz et al.

30 Metal-ligands comprise a central metal atom or ion surrounded by, associated with and/or bonded to other atoms, ions, molecules or compounds – collectively referred to as “ligands” – typically through a carbon (to form, e.g., an organometallic), nitrogen, phosphorous, sulfur or oxygen atom and/or one or more linker moieties. The

one or more ligands typically bind to one or more metal center and/or remain associated therewith, and by such association, modify the shape, electronic and/or chemical properties of the active metal center(s) of the metal-ligand complex. The ligands can be organic (e.g., ¹-aryl, alkenyl, alkynyl, cyclopentadienyl, CO, 5 alkylidene, carbene) or inorganic (e.g., Br⁻, Cl⁻, OH⁻, NO²⁻, etc.), and can be charged or neutral. The ligand can be an ancillary ligand, which remains associated with the metal center(s) as an integral constituent of the catalyst or compound, or can be a leaving group ligand, which may be replaced with an ancillary ligand or an activator component. Exemplary metals / metal ions include ions derived from, for example, 10 simple salts (e.g., AlCl₃, NiCl₂, etc.), complex or mixed salts comprising both organic and inorganic ligands (e.g., [(¹-5-C₅Me₅)IrCl₂]₂, etc.) and metal complexes (e.g., Gd(NTA)₂, CuEDTA, etc.), and can generally include, for example, main group metal ions, transition metal ions, lanthanide ions, etc.

Libraries of metal-ligand candidate materials can be prepared, for example, 15 according to the methods disclosed in PCT Patent Application WO 98/03521 of Weinberg et al. Briefly, a desired ligand can be combined with a metal atom, ion, compound or other metal precursor compound. In many applications, the ligands will be combined with such a metal compound or precursor and the product of such combination is not determined, if a product forms. For example, the ligand may be 20 added to a reaction vessel at the same time as the metal or metal precursor compound along with the reactants. The metal precursor compounds may be characterized by the general formula M(L)_n (also referred to as ML_n or M-L_n) where M is a metal and can include metals selected from the group consisting of Groups 5, 6, 7, 8, 9 and 10 of the Periodic Table of Elements. In some embodiments, M can be selected from the 25 group consisting of Ni, Pd, Fe, Pt, Ru, Rh, Co and Ir. L is a ligand and can be selected from the group consisting of halide, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, hydroxy, boryl, silyl, hydrido, thio, seleno, phosphino, amino, and combinations thereof, among others. When L is a 30 charged ligand, L can be selected from the group consisting of hydrogen, halogens, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno,

22

and combinations thereof. When L is a neutral ligand, L can be selected from the group consisting of carbon monoxide, isocyanide, nitrous oxide, PA₃, NA₃, OA₂, SA₂, SeA₂, and combinations thereof, wherein each A is independently selected from a group consisting of alkyl, substituted alkyl, heteroalkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, and amino. Specific examples of suitable metal precursor compounds include Pd(dba)₂ (dba = dibenzylideneacteone), Pd₂(dba)₃, Pd(OAc)₂ (Ac = acetate), PdCl₂, Pd(TFA)₂, (TFA = trifluoroacetate), (CH₃CN)₂PdCl₂, and the like. In this context, the ligand to metal precursor compound ratio is in the range of about 0.01:1 to about 100:1, more preferably in the range of about 0.5:1 to about 20:1. The metal atom, ion or metal precursor may be supported or not. Supports may be organic or inorganic. Similar to the ligands, the support may be an L. In other embodiments, the support will not form part of the metal precursor and suitable supports include silicas, aluminas, zeolites, polyethyleneglycols, polystyrenes, polyesters, polyamides, peptides and the like. Specific examples of Pd supported metals include Pd/C, Pd/SiO₂, Pd/CaCO₃, Pd/BaCO₃, Pd/aluminate, Pd/aluminum oxide, Pd/polystyrene, although any of the metals listed above could replace Pd in this list, e.g., Ni/C, etc. In other applications, the ligand will be mixed with a suitable metal precursor compound prior to or simultaneous with allowing the mixture to be contacted to the reactants. When the ligand is mixed with the metal precursor compound, a metal-ligand complex may be formed, which may be employed as a candidate material.

Non-biological organic materials include organic materials other than biological materials. Organic materials are considered to include compounds having covalent carbon-carbon bonds. Biological materials are considered to include nucleic acid polymers (e.g., DNA, RNA) amino acid polymers (e.g., enzymes) and small organic compounds (e.g., steroids, hormones) where the small organic compounds have biological activity, especially biological activity for humans or commercially significant animals such as pets and livestock, and where the small organic compounds are used primarily for therapeutic or diagnostic purposes. While biological materials are of immense commercial interest with respect to pharmaceutical and biotechnological applications, a large number of commercially significant applications involve chemical processes that are enhanced by other than

biological materials. Moreover, while fundamental screening approaches for many pharmaceutical and biological activities are known or readily adapted from known approaches, screening approaches for non-biological materials have not heretofore been widely investigated and reported. Although the candidate materials being 5 screened are preferably not, themselves, biological organic materials, the candidate materials of the invention (e.g., inorganic materials) can be employed to enhance reactions directed to producing a biological organic material as the product of a chemical reaction (e.g., materials that enhance chemical-based, non-enzymatic DNA synthesis, or materials that enhance a synthetic, non-enzymatic route to a particular 10 hormone or steroid).

In preferred applications, the candidate materials are catalysts being screened for catalytic activity and/or for catalytic selectivity for a chemical reaction of interest. The candidate catalysts can be homogeneous catalysts or heterogeneous catalysts. For 15 homogeneous catalysis, the candidate materials are preferably solids or liquids which are soluble or miscible in the reaction medium under the reaction conditions, but can also include gasses. For heterogeneous catalysis, the candidate materials are preferably solids. In general, homogeneous candidate catalyst materials and heterogeneous candidate catalyst materials can include organic, inorganic and metal-ligand catalysts such as are described above.

20 Exemplary reactions for which a homogeneous catalyst may be investigated pursuant to the present invention, as well as known homogeneous catalysts for such reactions are shown in Table 1A. Exemplary reactions for which a heterogeneous catalyst may be investigated pursuant to the present invention, as well as known heterogeneous catalysts for such reactions are shown in Table 1B. The library of 25 candidate catalysts being screened can be variations in the structure or composition of known catalysts or can be structurally unrelated thereto.

Table 1A: Exemplary Homogeneous Catalytic Reactions

	<u>Reaction Class</u>	<u>Known Catalyst</u>
5	asymmetric C-C double bond isomerization	Ru-, Rh- ligand (e.g., phosphine)
	Suzuki biaryl cross-coupling	Pd-ligand (e.g., phosphine)
	hydroformylation	Co-, Rh- ligand (e.g., phosphine,
10	phosphite)	
	hydrocarboxylation	Mo-, Pd-, Rh-, Co-, ligand (e.g.,
	phosphine)	
	Heck reaction	Pd-ligand (e.g., phosphine)
	hydrocyanation	Ni-ligand (e.g., phosphite)
	assymetric hydrogenation	Ru-, Rh- ligand (e.g., phosphine)
15	Friedel-Crafts reaction	HF, AlCl ₃
	olefin polymerization	Zr-, Ti-, Hf- ligand (e.g.
	cyclopentadiene)	
	olefin metathesis	Ni-, Pd- ligand (e.g., bis-imine)
	methanol carbonylation	Ru-, Mo- ligand (e.g., N-, P- based)
20	epoxide ring opening	Ir, Rh with halides (e.g., MeI, HI)
	halogen exchange reaction (e.g., Ar-Br → Ar-F)	Cu-ligand (e.g., alkoxide, amide, amine)
	hydrolysis (e.g., ethylene oxide → ethylene glycol)	R ₄ P ⁺ X ⁻ (X= halide)
25	alcoholysis (e.g. ethylene oxide → glycol ethers)	H ⁺ source (e.g., H ₂ SO ₄)
	ammonolysis	Alkali hydroxide, Al ₂ O ₃
	Heat (e.g., ethylene oxide → ethanolamines)	
30	dimerization	H ⁺ source
	(e.g. ethylene oxide → 1,4-dioxane)	
	carboxylation	Mineral acids (e.g., H ₂ SO ₄)
	e.g., Koch-Haaf reaction	Lewis acids (e.g., BF ₃ , SbF ₅)
	electrophilic aromatic substitutions (e.g., nitration, sulfonation)	Mineral and Lewis Acids
35	esterification (direct, trans, poly)	Metal ions (e.g., Zn, Cu, Pb, Mn, Cd, Na, Li, Hg, Fe, Ni, Co, Ca)
	halogenations (e.g. ethylene chlorination)	FeCl ₃
	isomerization	PhCN,CuCl
40	(e.g., 1,4-dichlorobutene → 3,4-dichloro-1-butene)	
	oxidative carbonylation	Pd + alkali iodide
	(e.g. Aniline → N-Phenethylurethane)	

Table 1B: Exemplary Heterogeneous Catalytic Reactions

	<u>Reactant(s)</u>	<u>Product</u>	<u>Known Catalyst</u>
5	ethylene+acetic acid	vinyl acetate	Pd-Au
	ethylene glycol	glyoxal	Cu
	ethylene	ethyleneoxide	Ag
10	methanol	formaldehyde	Ag
	butene dimerization	octene	Ni
	HCl	Cl2	Cu-Fe-Cl, Cu-Cr-O
	propylene	acrolein	Bi-Mo-O
	acrolein	acrylic acid	Mo-V-O (+ Cu-Mo-O + W-O +Fe-Mo-O)
15	methacrolein	methacrylic acid	POM
	o-xylene	Phthalic anhydride	V/TiO2
	butane	maleic anhydride	VPO
	toluene	benzonitrile	V-Sb-O, Fe-Sb-O, V2O5
20	ethylbenzene	styrene (non-ODH)	K-Fe-O
	ethylbenzene	styrene (ODH)	K-Bi-O/TiO2
	propane	propylene	K-Cr-O/Al2O3
	vinyl cyclohexene	styrene	Cu/zeolite
	cyclohexanol	cyclohexanone	Cu/SiO2
25	cyclohexene	benzene	NM/support
	cyclohexylamine	aniline	NM/support
	side chain aromatics	aromatic acids	Co-Mn-Zr-acetates (+Ce)
	ethylene	acetaldehyde	Pd-Cu, Pd-Au
	acetaldehyde	acetic acid	Mn-acetate
30	propylene	propylene oxide	Ti/silicalite
	butadiene	vinyl oxirane	Ag
	nitrobenzene	aniline	Cu/SiO2
	beta-picoline	nicotinic acid	V-Mo/Ti-Zr-O
	maleic anhydride	gamma-butyrolactone, tetrahydrofuran	
35	propane	acrylic acid	Cu-Zn-O, Cu-Cr-O
	propane	acryl nitrile	V-Mo-Nb-O (+Te) (+Bi) (Fe, Ce, Cr, Co)
	benzene	phenol	BiMoO, MoTeFeSbO
	syngas	methanol	Fe-Ga/zeolite
40	syngas	methane	Cu-Zn/Al2O3
	syngas	fuel hydrocarbons	Ni
	H2+N2	ammonia	Fe, Co
	CH4+H2O	H2+CO	Fe
	DeNOx		Ni
45			V/TiO2

The ionic liquids, catalysts, compositions and processes of this invention can be prepared and/or tested for in a combinatorial fashion. In this regard, the ionic

liquids, complexes or processes may be prepared and/or tested in rapid serial and/or parallel fashion, e.g., in a library or array format. When prepared in a library format, for example, the ionic liquids may take the form of one or more arrays comprising a plurality of compositions wherein each composition can be characterized by the 5 general formula A^+B^- with the definitions above applying to this formula.

In a combinatorial array, each of the plurality of compositions (e.g., each ionic liquid) is somehow different from the other compositions in the array. Such differences can be compositional (such as composition of ionic liquid or ratio of ionic liquid to other reaction media or catalyst composition or metal complex to activator 10 ratio or volume of solvent, etc.), processing parameters (such as temperature, pressure, atmosphere composition, etc.) or other differences that those of skill in the art will recognize from a review of this specification. Also typically, each composition in the array is at a selected region on a substrate such that each composition is isolated from the other compositions. This isolation can take many 15 forms, typically depending on the substrate used. If a flat substrate is used, there may simply be sufficient space between regions so that there cannot be interdiffusion between compositions. As another example, the substrate can be a microtiter or similar plate having wells so that each composition is in a region separated from other compositions in other regions by a physical barrier.

20 The array typically comprises at least 10 different compositions, e.g., 10 different ionic liquids or 10 different mixed solvent systems including an ionic liquid or etc. In other embodiments, there are at least 25 compositions on or in the substrate each having a different chemical formula. In still other embodiments, there are at least 50 or 96 or 124 or more compositions on or in the substrate. Because of the 25 manner of forming combinatorial arrays, it may be that each compound, material or composition is not pure. Typically, each compound, material or composition in the plurality is at least 50% pure within its region.

In still other embodiments, the library formed depends on how the desired reaction will be tested. For example, the libraries of this invention can be one or more 30 arrays of ionic liquids, monomers and/or comonomers, solvents, catalysts, metal-ligand complexes or activators. Thus, if the portion of the reaction that is to be studied in parallel is the difference between ionic liquids, an array of ionic liquids having different compositions in the plurality can be formed and then used keeping all

27

other conditions of the reaction constant. Similarly, reaction conditions, processes, reactants, catalysts or solvents can be varied in a known manner using one or more arrays of the present invention.

Thus, this invention provides arrays of ionic liquids where each member of the

5 array may be characterized by the general formula A^+B^- where A^+ represents any stable organic or inorganic cation and B^- represents any stable organic or inorganic anion. More specific definitions of A^+ and B^- are discussed above. The array can be formed in a plate that contain a plurality of vials, with each vial holding a member of the array of the ionic liquids, such that each member of the array cannot contact

10 another member of the array. Alternatively the arrays can be in titer plate format, such as in a microtiter plate so that one member of the array cannot contact another member of the array.

One combinatorial research application is a method of discovering ionic liquids useful for particular reactions with the steps of the method comprising:

15 providing an array of ionic liquids and running the reaction of interest in parallel using the ionic liquids in the array as a component in the reaction. The ionic liquid can be functioning in any of the capacities discussed above, such as the solvent, initiator, etc. Different ionic liquid compositions can be tested in the reaction of interest. Alternatively, each member of the array can contain the same ionic liquid

20 allowing for process conditions of the reaction to be varied within the array. An example of this is shown in Example 1 where different members in the array contain the same ionic liquid, but are tested in a polymerization reaction carried out at different temperatures.

In more specific embodiments, ionic liquids for the polymerization of

25 isoolefins or for the copolymerization of an isoolefin plus additional comonomer can be tested in a combinatorial manner. Here, an array of ionic liquids is provided with an aliquot of each member of the array being dispensed into a reactor block containing an array of reaction vessels. The reactor blocks discussed in the other incorporated patent applications and patents below can be used in this embodiment.

30 The common theme among them is a plurality of reaction vessels for temperature or pressure controlled experiments. The other components of the polymerization reaction are added to the reactor vessels (e.g., monomer, initiators, co-initiators, co-solvents, etc.) and the reaction is carried out at desired reaction conditions, which may be

varied between two or more arrays or within a single array. The order of addition of reaction components depends on the reaction being studied. As discussed above, other compounds may be added to the ionic liquid to form a new catalyst composition, which polymerizes an isoolefin or copolymerizes the isoolefin plus 5 additional comonomer. The preferred isoolefins are isobutylenes for creating polyisobutylenes.

The catalytic performance (activity and/or selectivity) of the compositions of this invention can be tested in a combinatorial or high throughput fashion. For any of the listed transformations, thin layer chromatography (TLC) in combination with 10 imaging technology may be employed or accelerated liquid chromatographic techniques or accelerated characterization techniques may be used.. TLC is well known in the art, see for example Vol. 1, *Thin-Layer Chromatography, Reagents & Detection Methods*, Jork et al. (VCH Publishers, New York, New York 1990), incorporated herein by reference. For accelerated liquid chromatographic, gel 15 permeation chromatography and other techniques, see provisional U.S. patent application no. 60/080,652, filed April 3, 1998, incorporated herein by reference. Polymerizations, oligomerizations and other reactions can also be performed in a combinatorial fashion, see, e.g., commonly owned U.S. Patent Application No. 09/177,170, filed October 22, 1998 (having Attorney Docket No. 65304-044), herein 20 incorporated by reference. As shown in the examples of this specification, the reactions can be carried out under different reaction conditions, including temperature using a temperature controlled reactor block to hold the polymerization reactors. See commonly owned U.S. Patent Application No. 09/417,125, filed November 19, 1998 (having attorney docket no. 65304-014), incorporated herein by reference. High 25 throughput screening can also be performed rapidly and/or optically and/or in parallel, for example, as disclosed in commonly owned U.S. Patent Applications 09/067,448, filed April 2, 1998, 08/947,085, filed October 8, 1997, 09/113,171, filed August 12, 1998, and 08/946,135, filed October 7, 1997, each of which is incorporated by reference.

EXAMPLES

When necessary, experiments were carried out in an inert atmosphere using nitrogen or argon as the inert gas and following practices standard to those of skilled in the art for these types of reactions (for example, see Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*, 2nd ed. (New York : Wiley, c1986)).

5 Except where noted, all starting compounds and solvents were obtained from J.T. Baker, Inc. or Aldrich and used without further purification. Dry solvents were obtained from Aldrich in Sure-Seal™ bottles and used without further purification. Deuterated solvents were purchased from Aldrich or Cambridge Isotopes, Inc. and used as is or dried according to standard procedures published in Perrin, D. D.;

10 Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd Ed.; Pergamon: New York, 1989.

The following polymerization examples were performed in a 96 well parallel reactor containing 96 individually stirred 1 ml glass vials. The reactor was a series of 15 wells in a modular block that is described in U.S. Patent Application No. 09/417,125, filed November 19, 1998 (having attorney docket no. 65304-014). Thus, libraries of 96 polymerization reactions were examined in parallel.

Example 1/Library 1

20 In this example, an ionic liquid was used as a catalyst for the polymerization of isobutylene. The ionic liquid chosen for this library was 1-methyl-3-ethylimidazolium aluminum tetrachloride. The following 12 x 8 library was created by dispensing the following volumes of ionic liquid (Table 1) and isobutylene (Table 2) in microliters into the cryogenic reactor described above in the 25 order presented (i.e., ionic liquid first and isobutylene last). Reaction temperatures were varied across the columns only (indicated by T = above columns 1-8, given in degrees centigrade).

Table 1: Ionic Liquid Volumes (μ l)

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	10	10	10	10	10	10	10	10
11	20	20	20	20	20	20	20	20
10	30	30	30	30	30	30	30	30
9	40	40	40	40	40	40	40	40
8	50	50	50	50	50	50	50	50
7	60	60	60	60	60	60	60	60
6	70	70	70	70	70	70	70	70
5	80	80	80	80	80	80	80	80
4	90	90	90	90	90	90	90	90
3	100	100	100	100	100	100	100	100
2	150	150	150	150	150	150	150	150
1	200	200	200	200	200	200	200	200

5

The volumes of isobutylene dispensed into this library are shown below.

Table 2: Isobutylene Volumes (μ l)

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	483	483	483	483	483	483	483	483
11	461	461	461	461	461	461	461	461
10	439	439	439	439	439	439	439	439
9	418	418	418	418	418	418	418	418
8	396	396	396	396	396	396	396	396
7	374	374	374	374	374	374	374	374
6	352	352	352	352	352	352	352	352
5	330	330	330	330	330	330	330	330
4	308	308	308	308	308	308	308	308
3	286	286	286	286	286	286	286	286
2	400	400	400	400	400	400	400	400
1	400	400	400	400	400	400	400	400

The reaction temperature was set to -30°C by setting the cryogenic reactor.

10 After this setup, (i.e., following the addition of the isobutylene), the reaction was stirred for 1 hour whereupon the reaction was quenched with 30 microliters of ethanol. The reactor was opened up and the polymer from each library element was analyzed by rapid molecular weight gel permeation chromatography described in provisional U.S. patent application no. 60/080,652, filed April 3, 1998, incorporated herein by reference. The polymer yields and molecular weights are given below in Tables 3 and 4, respectively.

15

Table 3: Approximate Polymer Yields (given as percentages)

Row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	15	21	38	50	33	43	36	45
11	21	21	36	34	49	56	51	23
10	30	30	69	58	66	52	59	35
9	30	33	48	42	48	33	51	41
8	37	36	45	50	35	55	44	45
7	32	48	52	54	29	60	40	41
6	25	41	47	69	46	54	39	56
5	33	45	49	62	48	44	64	54
4	37	45	46	50	36	45	53	52
3	39	59	60	61	37	52	59	35
2	25	40	35	34	18	31	25	50
1	26	21	6	38	45	41	7	45

5 Table 4: Weight Average Molecular Weights

row/column	1	2	3	4	5	6	7	8
	T = -65	T = -65	T = -40	T = -40	T = -30	T = -30	T = -20	T = -20
12	66177	55468	526040	459950	302930	279870	116900	128060
11	60525	62186	503530	542320	304270	294820	120210	149450
10	930990	1032400	469940	517090	242660	289620	136570	141150
9	44152	46565	496040	511850	283400	304900	132130	158630
8	47410	44481	454700	512700	298200	302860	146610	146980
7	54803	48026	477890	503930	275940	241820	154920	160970
6	49543	48588	486100	509290	317170	302410	176400	153210
5	49771	43407	519060	461980	308430	312630	151980	141350
4	50672	44568	526990	487590	309750	297850	172690	163300
3	57416	42827	380190	466720	276400	280260	155010	148590
2	46973	44870	417900	259820	292350	247920	119080	72881
1	49798	47867	NA	405330	160910	146460	142250	80078

NA = Data Not available.

Example 2/Library 2

10 The following example represents the case where a catalyst was added to an ionic liquid to produce a new catalyst composition for the polymerization of isobutylene. The catalyst chosen for this library was ethylaluminum dichloride dispensed as a 1M solution in hexane. The polymerization was performed in hexane. The ionic liquid chosen for this library was 1-methyl-3-ethylimidazolium aluminum tetrachloride. The following 12 x 8 library was created by dispensing the following 15 volumes of ionic liquid (Table 5), ethylaluminum dichloride (Table 6), hexane (Table 7) and isobutylene (Table 8) in microliters into the cryogenic reactor described above

32

in the order presented (i.e., ionic liquid first, ethylaluminumdichloride second, hexane third and isobutylene last).

Table 5: Ionic Liquid Volumes (μL)

row/column	1	2	3	4	5	6	7	8
12	10	10	10	10	10	10	10	10
11	20	20	20	20	20	20	20	20
10	30	30	30	30	30	30	30	30
9	40	40	40	40	40	40	40	40
8	50	50	50	50	50	50	50	50
7	60	60	60	60	60	60	60	60
6	70	70	70	70	70	70	70	70
5	80	80	80	80	80	80	80	80
4	90	90	90	90	90	90	90	90
3	100	100	100	100	100	100	100	100
2	50	50	50	50	100	100	100	100
1	0	0	0	0	0	0	0	0

5

Table 6: Volume of Ethylaluminumdichloride (μL of 1M solution in hexane)

row/column	1	2	3	4	5	6	7	8
12	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0
10	11	23	34	46	11	23	34	46
9	11	23	34	46	11	23	34	46
8	11	23	34	46	11	23	34	46
7	11	23	34	46	11	23	34	46
6	11	23	34	46	11	23	34	46
5	11	23	34	46	11	23	34	46
4	11	23	34	46	11	23	34	46
3	11	23	34	46	11	23	34	46
2	11	23	34	46	11	23	34	46
1	11	23	34	46	11	23	34	46

Table 7: Volume of Hexane (μl)

row/column	1	2	3	4	5	6	7	8
12	372	372	372	372	350	350	350	350
11	362	362	362	362	340	340	340	340
10	341	330	318	307	318	307	296	284
9	331	320	308	297	308	297	286	274
8	321	310	298	287	298	287	276	264
7	311	300	288	277	288	277	266	254
6	301	290	278	267	278	267	256	244
5	291	280	268	257	268	257	246	234
4	281	270	258	247	258	247	236	224
3	271	260	248	237	248	237	226	214
2	321	310	298	287	248	237	226	214
1	371	360	348	337	348	337	326	314

5 Table 8: Volume of Isobutylene (μl)

row/column	1	2	3	4	5	6	7	8
12	25	25	25	25	51	51	51	51
11	25	25	25	25	51	51	51	51
10	25	25	25	25	51	51	51	51
9	25	25	25	25	51	51	51	51
8	25	25	25	25	51	51	51	51
7	25	25	25	25	51	51	51	51
6	25	25	25	25	51	51	51	51
5	25	25	25	25	51	51	51	51
4	25	25	25	25	51	51	51	51
3	25	25	25	25	51	51	51	51
2	25	25	25	25	51	51	51	51
1	25	25	25	25	51	51	51	51

The reaction temperature was set to -30 °C by setting the cryogenic reactor.

After this setup, (i.e., following the addition of the isobutylene), the reaction was 10 stirred for 1 hour whereupon the reaction was quenched with 30 microliters of ethanol. The reactor was opened up and the polymer from each library element was analyzed as in Example 1. The polymer yields and molecular weights are given below in Tables 9 and 10, respectively.

15

Table 9: Approximate Polymer Yields (given as percentages)

Row/column	1	2	3	4	5	6	7	8
12	100	100	100	100	67	100	100	100

11	100	100	100	45	100	100	100	100
10	100	100	100	100	100	100	100	100
9	100	100	100	100	100	100	100	100
8	100	100	100	79	100	100	100	58
7	100	100	100	100	100	100	100	31
6	100	100	100	100	84	100	90	63
5	100	100	100	17	100	100	100	32
4	100	100	100	88	30	100	100	NA
3	NA	100	100	100	NA	100	100	NA
2	100	100	100	98	NA	100	100	NA
1	79	81	78	75	83	78	67	65

NA = Data Not Available

Table 10: Weight Average Molecular Weights

row/column	1	2	3	4	5	6	7	8
12	416250	384080	203760	515670	141300	110710	298250	217320
11	80309	66451	335600	421650	362990	299750	269390	220620
10	285220	61764	39044	51026	70941	39414	103730	109340
9	261320	222200	55577	73895	69419	46013	NA	142190
8	275590	235030	186310	250930	139960	145490	NA	191860
7	228140	188120	204440	228230	NA	123380	123350	176520
6	247290	211960	212890	250480	NA	135610	112070	163940
5	247860	201270	193620	202110	132010	121370	88619	162380
4	NA	230990	191740	202030	145570	118040	100270	139530
3	NA	209270	197170	167340	139230	147100	124360	108010
2	NA	224520	212170	193060	NA	147990	111690	149740
1	NA	196050	207050	205720	286190	112710	123920	132260

5

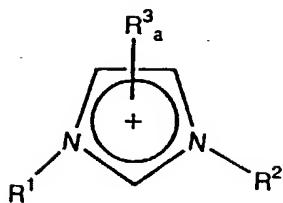
NA = Data Not Available

It is to be understood that the above description is intended to be illustrative
10 and not restrictive. Many embodiments will be apparent to those of skill in the art
upon reading the above description. The scope of the invention should, therefore, be
determined not with reference to the above description, but should instead be
determined with reference to the appended claims, along with the full scope of
equivalents to which such claims are entitled. The disclosures of all articles and
15 reference, including patent application and publication, are incorporated herein by
reference for all purposes.

What is claimed is:

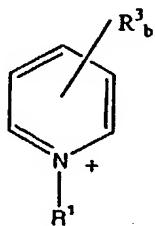
1. An array comprised of a plurality of members with each member comprising an ionic liquid characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion.
5
2. The array of claim 1 wherein A^+ is a stable cationic molecule that is created by alkylation of a compound selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, 10 oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, 15 piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines.
15
3. The array of claim 1 wherein A^+ is a stable cationic molecule that is created by protonation or acylation of a compound selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, 20 oxazines, oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophens, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophens, dibenzothiophens, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, 25 piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines.
25

4. The array of claim 1 wherein A^+ can be characterized by the general formula:



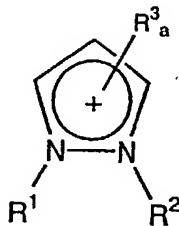
5 where R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2 or 3 signifying the number of R^3 groups attached to a carbon atom of the ring.

5. The array of claim 1 wherein A^+ can be characterized by the general formula:



15 where R^1 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and b is 0, 1, 2, 3, 4 or 5 signifying the number of R^3 groups attached to a carbon atom of the ring.

6. The array of claim 1 wherein A^+ can be characterized by the general formula:



5 where R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; and a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring.

10

7. The array of claim 1 where A^+ can be characterized by the either of the general formulas: $R^1R^2R^3R^4N^+$ or $R^1R^2R^3R^4P^+$ where each of R^1 , R^2 , R^3 and R^4 is independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

15

8. The array of claim 1 where A^+ is an acyclic organic compound capable of being converted into a stable organic cation, and the acyclic compound is selected from the group consisting of amines, phosphines, arsines, stibines, ethers, thioethers and selenoethers.

20

9. The array of claim 1 wherein B^- is represented by the general formula $AlR_{4-z}X_z$ where R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl,

25

alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; X is selected from the group of halogens; and z is 0, 1, 2, 3 or 4.

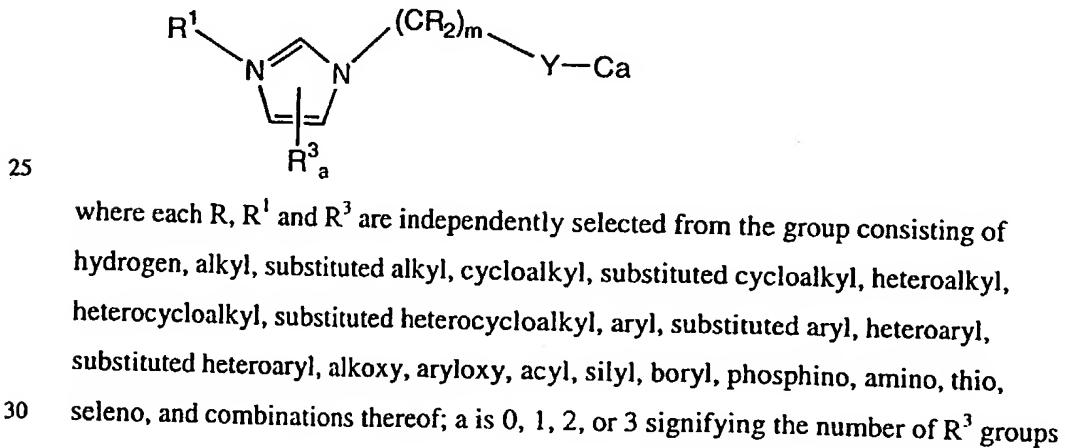
10. The array of claim 1 wherein B^- may be selected from the group consisting of halide ions, JX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , JR_4^- , AlU_4^- , $Al_2U_7^-$, OAc^- substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, borates, carbonates, substituted or unsubstituted carboxylates and triflates; and wherein J is boron and R is selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

11. The array of claim 1, wherein each member of the array additionally comprises either a catalyst or an initiator.

12. The array of claim 1, wherein at least one member of the array comprises a group that can act as a catalyst or scavenger and said group is covalently bonded to either A^+ or B^- .

20

13. The array of claim 13, wherein said group is attached directly to the cationic portion of the ionic liquid, so that A^+ may be represented by the following general formula:



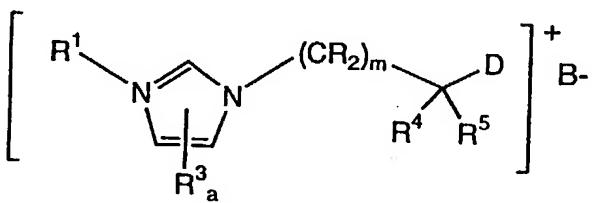
attached to a carbon atom of the ring; m is an integer from 1-50; Y is any functional group capable of binding the catalyst, initiator or scavenger; and Ca is the catalyst or scavenger.

5

14. The array of claim 13, wherein said group is covalently bonded to B⁻.

15. The array of claim 1, wherein each member of the array may be characterized by the general formula:

10



15

where R, R¹, R³, R⁴ and R⁵ are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R³ groups attached to a carbon atom of the ring; m is an integer from 1-50; and D is selected from the group consisting of halogen, SCN, CN, OH, OR, OCOR, COOR, O₂SR.

20

16. The array of claim 1, wherein there are at least 10 members in the array and said 10 members are different from each other.

17. The array of claim 17, wherein said difference is a difference in composition of the ionic liquid.

25

18. The array of claim 17, wherein said difference is a ratio of ionic liquid to other reaction media.

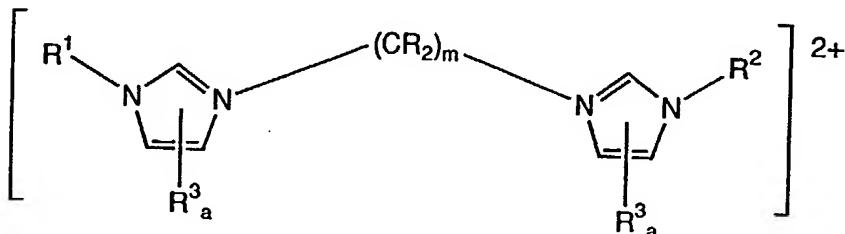
19. The array of claim 17, wherein said difference is selected from the group consisting of temperature, pressure, solvent and atmosphere.

20. The array of claim 17 wherein there are at least 25 members in
5 the array that are different from each other.

21. An array comprised of a plurality of members with each member comprising an ionic liquid characterized by one of the general formulas $A^{n+} B^{n-}$, $A^{n+} nB^-$ or $nA^+ B^{n-}$ where n is any positive integer greater than 1 and where A^+
10 represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion.

22. The array of claim 21, wherein A^+ may be represented by the following general formula:

15



where n is 2; R, R^1 , R^2 and R^3 are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, 20 substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R^3 groups attached to a carbon atom of the ring; and m is an integer from 1-50.

23. The array of claim 22 wherein the CR_2 is replaced with a
25 compound selected from the group consisting of substituted alkyls and substituted aryl.

24. The array of claim 21, wherein at least one member of said array additionally comprises a second ionic liquid characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion.

5

25. A process for the combinatorial testing an ionic liquid for suitability in a reaction, comprising:

mixing at least a portion of members of an array having a plurality of members, where each member comprises at least one ionic liquid
10 characterized by the general formula A^+B^- where A^+ represents any stable inorganic or organic cation and B^- represents any stable organic or inorganic anion, with one or more potential catalysts in a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members; and

15 subjecting said plurality of reactor vessels to reaction conditions that cause a reaction in at least one of said plurality of reactor vessels.

26. The process of claim 25, wherein said reaction conditions are polymerization conditions comprising a temperature in the range of from -100°C to
20 300°C , at least one monomer that is an isobutylene and an inert atmosphere.

27. The process of claim 25, wherein said catalyst is an organometallic catalyst.

25 28. The process of claim 25 wherein A^+ is a stable cationic molecule selected from the group listed in any of claims 2, 3, 4, 5, 6, 7 or 8.

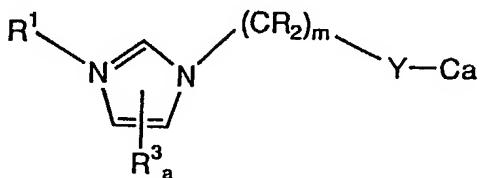
29. The process of claim 25 wherein B^- is selected from the group consisting those molecules listed in any of claims 9 or 10.

30

30. The process of claim 25 wherein at least one member of said plurality of ionic liquids contains a group that can act as a catalyst, initiator or scavenger and said group is covalently bonded to either A^+ or B^- .

31. The process of claim 30 wherein said group is attached directly to the cationic portion of the ionic liquid, so that A^+ may be represented by the following general formula:

5

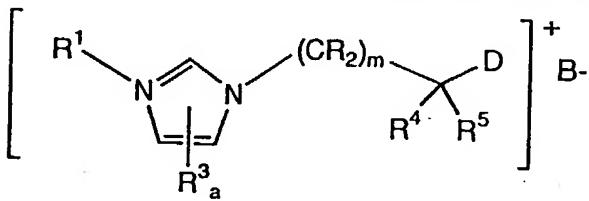


where each R, R¹ and R³ are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl,

10 substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R³ groups attached to a carbon atom of the ring; m is an integer from 1-50; Y is any functional group capable of binding the catalyst, initiator or scavenger; and Ca is the catalyst, initiator or scavenger.

15

32. The process of claim 25 wherein at least one member of said array of ionic liquids may be characterized by the general formula:



20 where R, R¹, R³, R⁴ and R⁵ are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R³ groups attached to a carbon atom of the ring; m is an integer from 1-50; and D is selected from the group consisting of halogen, SCN, CN, OH, OR, OCOR, COOR, O₂SR.

25

33. The process of claim 25, wherein at least one member of said array of ionic liquids is part of a two or more phase solvent system and another portion of said solvent system comprises a solvent selected from the group consisting of alkanes, cycloalkanes, Isopar E® and combinations thereof.

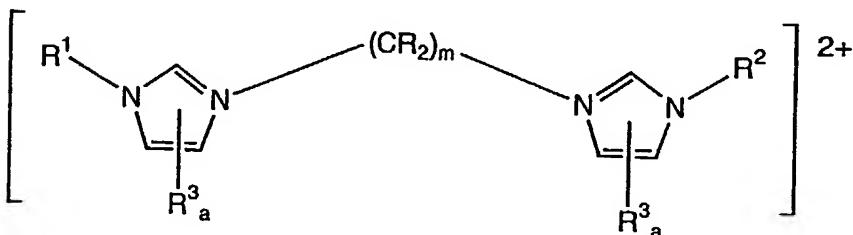
34. A process for combinatorial testing an ionic liquid for suitability in a reaction, comprising:

10 providing an array of ionic liquids having a plurality of members, where each member can be characterized by one of the general formulas $A^{n+} B^{n-}$, $A^{n+} nB^-$ or $nA^+ B^{n-}$ where n is any positive integer greater than 1 and where A^+ and A^{n+} represents any stable inorganic or organic cation and B^{n-} and B^- represents any stable organic or inorganic anion;

15 dispensing at least a portion of said plurality of members into a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members; and

subjecting said plurality of reactor vessels to reaction conditions that cause a reaction in at least one of said plurality of reactor vessels.

20 35. The process of claim 34, wherein A^{n+} may be represented by the following general formula:



25 where n is 2; R, R¹, R² and R³ are independently selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, silyl, boryl, phosphino, amino, thio, seleno,

and combinations thereof; a is 0, 1, 2, or 3 signifying the number of R³ groups attached to a carbon atom of the ring; and m is an integer from 1-50.

36. The process of claim 35, wherein the CR₂ is replaced with a
5 compound selected from the group consisting of substituted alkyls and substituted aryl.

37. A process for combinatorial testing an ionic liquid for suitability in a reaction, comprising:

10 providing an array of ionic liquids having a plurality of members, where each member can be characterized by the general formula A⁺B⁻ where A⁺ represents any stable inorganic or organic cation and B⁻ represents any stable organic or inorganic anion;

15 dispensing at least a portion of said plurality of members into a parallel reactor having a plurality of reactor vessels corresponding to said plurality of said members;

subjecting said plurality of reactor vessels to conditions that cause a reaction in at least one of said plurality of reactor vessels; and
20 wherein said reaction is selected from the group consisting of cross-coupling, Friedel-Crafts, dimerization, oligomerization, polymerization, hydrogenation, oxidation, dehydrogenation, aromatization, carbonylation, dehydrodimerization, hydrodehalogenation, hydrodesulfurization, oxychlorization, C-C coupling, Heck reaction, amination, amoxidation, alkylation, vinylation, acetoxylations, oxidative esterification, telomerization, hydroxylations of C=C bonds and aromatics, CH
25 hydroxylation, oxidative cleavage, epoxidation, reduction, hydrosilylation and hydroformylation.